

ADSORPTION OF METHYL ALCOHOL
FILMS ON ROCK SALT

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ABSTRACT

The optical method of Rayleigh and Drude as recently modified by Frazer and Herzfeld has been applied to the study of methyl alcohol films on rock-salt. The isothermal adsorption has been studied at pressures ranging from 10^{-5} mm to 11 cm mercury. The results indicate that a unimolecular layer is formed at a pressure between 10^{-5} and 10^{-4} mm of mercury, with no further adsorption until the region of 2-3 cm, when a second layer begins to form, with completion at 9-10 cm. The thickness of these layers is calculated to be in the neighborhood of 4.5-5.0Å. The effect of thorough outgassing has been observed and the results have been interpreted to indicate that with decrease in temperature either an underlying unimolecular layer of water vapor is formed, or that there is a true increase in the natural ellipticity of the surface. In addition, it is possible to calculate the isothermal heat of adsorption from the experimental data.

INTRODUCTION

IF A beam of light be allowed to fall upon a plane surface of a transparent medium at the polarizing angle, the reflected beam is not found to be completely plane polarized, but is always elliptically polarized. Drude¹ has shown that the ellipticity of the reflected beam may be explained by assuming that there is not a perfectly sharp boundary between the two media, but that there is present a transition layer whose properties vary from the rare to the dense medium. This sheet whose index of refraction gradually changes from the value of 1 (assuming the 1st medium to be air or vacuum) to n , the refractive index of the 2nd substance, is known as the transition layer. Drude has worked out the equation which yields the relation between the observed ellipticity and the thickness of the transition layer; where we define as the ellipticity the ratio of the amplitudes of the minor and major axes of the ellipse of polarization.

The result is as follows:

$$\rho = \frac{\pi}{\lambda} \frac{(\epsilon_1 + \epsilon_2)^{1/2}}{\epsilon_1 - \epsilon_2} \int \frac{(\epsilon - \epsilon_1)(\epsilon - \epsilon_2)}{\epsilon} dz \quad (1)$$

where ρ is the ellipticity, ϵ_1 , ϵ and ϵ_2 are the dielectric constants of the first, the transition, and the second media respectively, λ the wave-length of the incident light, and z the position in the transition layer.

It is possible to determine a lower limit for the value of the thickness of the layer, L , which will not deviate very greatly from its true value. For a

¹ Drude, Theory of Optics, p. 287, Longmans (1901).

given value of ρ it is evident that L will attain its smallest value when ϵ is assumed to be a constant whose value is determined by making the factor $(\epsilon - \epsilon_1)(\epsilon - \epsilon_2)/\epsilon$ a maximum. This condition will be fulfilled when $\epsilon = (\epsilon_1 \epsilon_2)^{1/2}$. Setting the refractive index equal to the square root of the dielectric constant, the expression for the lower limit of L becomes:

$$\frac{L_{min}}{\lambda} = \frac{\rho}{\pi(1 + n^2)^{1/2}} \frac{n + 1}{n - 1} \quad (2)$$

where n is the refractive index of medium 2 with respect to medium 1.

Work by Langmuir, and later by Eucken, has formed the background for the theory that adsorption takes place in uniform monomolecular layers, and that each layer is completed before the formation of a subsequent one. Many other workers have substantiated this theory. However, many experimenters have worked with glass surfaces, with the resultant difficulty that it is very hard to describe the exact condition of the surface; to say nothing of the elaborate set-up required for the volumetric measurements on such large surfaces. Now, an adsorbed film fulfills the condition of Drude's transition layer. So, by taking a small cleavage surface of a crystal (two or three millimeters square was found to be quite large enough) which reflects nearly as well as plate glass, it is possible to calculate directly the thickness of the adsorbed layer by observing the changes in the ellipticity of the reflected light. The materials selected for this experiment were rock-salt for the transparent medium, because of the relative ease with which a perfectly clean surface may be prepared; and methyl alcohol for the vapor, because of the insolubility of rock-salt.

The equations of Drude require that the amplitude of the incident light in the plane of incidence be equal to the amplitude in the direction perpendicular to the plane of incidence. In early work on the measurement of thin films by Drude¹ and Rayleigh² the incident light is polarized at an angle of 45° at the plane of incidence. The ellipticity was measured by means of a Babinet compensator. Other investigators; Ives and Johnsrud³ and Ellerbroeck,⁴ have measured films; but in no case with an accuracy greater than several Angstrom units. The method has been considerably improved in this laboratory by Herzfeld and Frazer,⁵ and an accuracy of 3/10 to 4/10 Å has been attained. The essential improvements are: (1) the incident light is unpolarized, giving greater intensity while fulfilling the conditions set by the theory. (2) the ellipticity is measured photometrically with an accuracy unobtainable with a compensator. The present apparatus is very similar to that used by the above mentioned authors, with a few added refinements, particularly in the photometric arrangement.

The apparatus is shown diagrammatically in Fig. 1. The source of light was an Ediswan 500 C. P. Pointolite which gives a very intense beam that is

² Rayleigh, *Phil. Mag.* [6] 23, 431 (1903).

³ Ives and Johnsrud, *Journal of the Optical Soc.* 15, 374 (1927).

⁴ Ellerbroeck, *Arch. Neerland Sci.* 111, A10, 42-90 (1927).

⁵ Frazer, *Phys. Rev.* 33, 99 (1929).

quite uniform. After passing through a pin hole S_1 , the image of the hot tungsten plate was brought to a focus on a second pin hole S_2 and the beam made parallel by lens L_3 . A piece of clean plate glass M_1 was placed at a very slight angle to the beam, the transmitted light being allowed to fall upon the crystal and the reflected beam being used as the comparison beam in the photometer. The transmitted beam was reflected from the crystal R at the polarizing angle, passed through the analyzing nickel and brought to focus upon a piece of lightly ground glass G_1 . This serves to produce a very uniform field in the photometer. The beam is then made parallel by a lens L_5 , is passed by the edge of the mirror M_3 through the photometer P and the filter A , to the eye. The comparison beam was reflected successively from the mirrors M_1 and M_2 , brought to focus upon a bit of ground glass G_2 which formed a pin hole S_3 ; behind this was placed the photometric wedge W . The beam is again made parallel, and is reflected from the photometer mirror M_3 through the filter A to the eye.

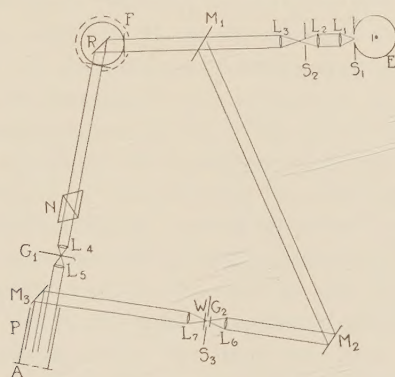


Fig. 1. Diagram of apparatus.

The photometer was of the Pfund split-field type, which consists of a mirror of a very sharp edge, set at an angle of 45° to the incident beams. One ray passes by the edge of the mirror and the other is reflected by it. The wedge was selected to give a linear transmission curve between ten percent and sixty percent; and was neutral as far as could be determined spectrophotometrically. In addition, screens were used which were calibrated against the wedge, and checked upon the same spectrophotometer. Inasmuch as the wave-length enters Drude's formula it is necessary to use a color filter. For this purpose, an aniline solution was found to be preferable to a monochromator since the intensity of the transmitted light is much greater. Such a solution was prepared by Professor Pfund, and the spectral centroid (5550A) calculated to an accuracy of about one percent.

The vacuum system itself merits a brief description. To prevent, as far as possible, contamination by stop-cock grease and occluded water vapor, a tube of activated coconut charcoal was placed between the crystal container and the rest of the system. The charcoal was previously outgassed by repeated heating to a dull red heat until no further gas was driven off. To make

certain that there was no backing-up on the far side of the charcoal plug, and auxiliary tube was connected to the container after the end of the main experiment. Pressure readings were found to be the same on both sides of the charcoal. The alcohol is kept in a trap and the vapor admitted as desired through a small stop-cock which was kept on the far side of the charcoal. The low pressures were read on a McLeod gauge. This was believed to be reliable as the pressure difference in the gauge at the highest pressures read was only 1.5 centimeters of mercury which is considerably below condensation pressure. As for occlusion of gases in the capillaries of the gauge, it was found that repeated pressure readings were quite consistent, so that it was not likely that our readings were affected. Higher pressures were read on the manometer.

EXPERIMENTAL PROCEDURE

The experimental procedure was as follows: a piece of rock-salt which was free of cloudiness was ground and polished along one edge at an angle of about 20° to the nearest cleavage plane. It was then cracked along the nearest cleavage direction and placed immediately in the container at the polarizing angle; and the apparatus was evacuated immediately. The polishing of the back plane at this angle of 20° removed entirely any reflection from the rear surface which would have vitiated our readings. The bottle containing the crystal was then heated and pumped out at a fairly good vacuum, 10^{-5} millimeters of mercury, for some hours. Methyl alcohol was admitted and the pressure noted; the nicol prism was set for minimum and maximum transmission, and the square root of the ratio of the readings gave the value of ρ . The temperature was measured and kept constant to within 5°C . The pressure was varied, and the readings taken again. This was repeated until the whole range between 10^{-5} mm and 11 cm had been covered. The temperature was then raised to the desired value, and the set of readings repeated. The alcohol was supplied by the Chemistry Department; no traces of water vapor or of any volatile organic substances were listed among the impurities.

Certain precautions were found to be quite necessary; (1) It is exceedingly important that no water vapor be present to be adsorbed on the surface; (2) No stop-cock grease or metal should be used in the set up as they might contaminate the surface; (3) The windows of the outfit must be free of double refraction; (4) The pressure in the gauge has to be corrected to give the pressure in the container as there is a temperature difference. As for the first precaution, it is impossible to state at present whether or not all traces of water vapor can be removed, even by continued heating at temperatures around 325°C . This will be discussed more fully at the end of the article. The second contamination was avoided more readily. The crystal was imbedded in a bead of molten silver chloride at the end of a glass rod, and the upper end of the rod was ground nicely to fit into a tube; no lubricant was used. This arrangement permitted very easy adjustment of the angle of reflection, and after the crystal was set at the polarizing angle, the tube was

sealed off. The windows were of Pyrex plate glass, which were very carefully annealed and tested between crossed nicols after being sealed to the container. To further test for double refraction a specimen was taken and its ellipticity determined in air and in the apparatus. The two values were identical. Knudsen's equation for the relative pressures on the two sides of a porous plug at absolute temperatures T_1 and T_2 respectively, is:

$$\frac{p_1}{p_2} = \frac{T_1^{1/2}}{T_2^{1/2}} \quad (3)$$

This equation fits our condition fairly closely for low pressures, and the correction was applied to all our low pressure readings; at high pressures the temperature correction is small enough to be neglected.

It was found possible to read the photometer to an accuracy of two percent. Accordingly, a group of eight or nine settings was taken for each reading, so that the probable error was quite close to one percent. Now,

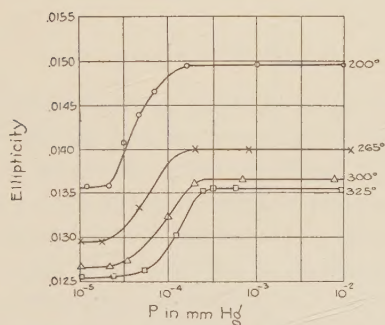


Fig. 2. Adsorption isotherms.

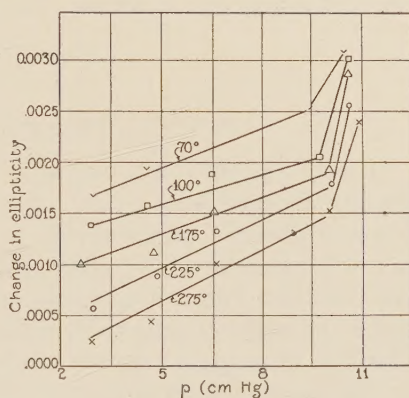


Fig. 3. Adsorption isotherms.

for $\lambda = 5550\text{\AA}$, a value of $\rho = 0.01$ means a layer about $45\text{\AA}$ thick. The values of ρ range from 0.0125 to 0.0170, so that the absolute error was about $0.5\text{\AA}$. This is the same percentage error, but a slightly larger absolute error than is claimed by Frazer.⁵ In all cases the adsorption is found to be completely reversible, and an adsorbed layer can be removed at will, returning the surface to its original condition.

EXPERIMENTAL RESULTS

At 325°C and 10^{-5} mm pressure the ellipticity had a value of 0.01265. The value remained unchanged at twice this pressure and then increased to a value of 0.01365 at 2×10^{-4} mm from this pressure up to the neighborhood of 2 cm there was no further change in the ellipticity. From this point, the value increased linearly until 9.5–10 centimeters was reached, after which there was an abrupt increase in the ellipticity. The isothermal corresponding to 300°C showed a very similar curve, parallel and higher than the one at 325°C . At 10^{-5} mm the value was 0.0127, and above 10^{-4} mm the value was

0.0137. The same flat region extending to two or three centimeters was noticed, and the following portion proceeded as in the first case. The curves were repeated for intervals down to 75°C. In all cases the adsorption at lower pressures occurred roughly between 10^{-5} mm and 10^{-4} mm, and in all cases there was no further change until the neighborhood of two to three centimeters had been reached. Further, the ellipticity following two centimeters proceeded regularly until ten centimeters was reached. These curves are shown in Figs. 2 and 3.

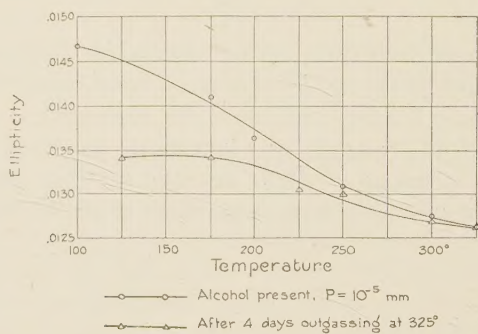


Fig. 4. Ellipticity as function of temperature. ($p=10^{-5}$ mm)

Lastly, the outfit was outgassed and the pressure was lowered to 10^{-5} mm, the temperature being 325°C. The pressure was kept constant and the temperature lowered progressively to 70°C, with readings being observed at intervals of about 50°C. The apparatus was then heated for three days at 325°C and 10^{-5} mm; it was then cooled over-night. Following, it was heated under the same conditions continuously throughout a period of four days. Readings were again taken at various temperatures as the cooling progressed. As will be seen from Fig. 4 at 325 degrees, the two curves coincide; their divergence is noticeable at 250°C, while at 100°C the increase in ellipticity for the clean surface in air is about 0.0008, and the corresponding increase for the surface in the presence of methyl alcohol is 0.00205.

INTERPRETATION AND DISCUSSION

The results of the preceding section are summarized in the following table:

Temp.	$\Delta\rho_1$	$\Delta\rho_2$	L_1	L_2
325	0.0009		4.1A	
300	.00095		4.3	
275	.0011	.0011	4.9	4.9A
225		.0012		5.4
200	.0014		6.3	
175		.0009		4.1
100		.0008		3.6
75		.0008		3.6

Where $\Delta\rho_1$ is the change in ellipticity in the approximate interval of 10^{-5} to 10^{-4} mm and $\Delta\rho_2$ the change in ellipticity in the approximate interval of

2–10 cm; L_1 and L_2 are the respective thicknesses in Angstroms corresponding to $\Delta\rho_1$ and $\Delta\rho_2$. The average value of L_1 is 4.9A, and the average value of L_2 is 4.3A. These values agree fairly well with values calculated by means of the kinetic theory. Pictorially, this means that the first layer of methyl alcohol molecules first begins to be adsorbed on the surface at pressures slightly above 10^{-5} mm, and that the layer is complete at pressures slightly above 10^{-4} mm. The alcohol molecule is probably oriented with its long axis perpendicular to the surface, with the OH radical adjacent to the Na ions of the lattice. From the pressure of about 10^{-4} mm until the region of 2–3 centimeters there is no further adsorption. At this point the formation of a second layer commences, and becomes complete at around 9.5–10 cm. Whether or not the second layer is oriented cannot be said definitely, as the binding forces must be considerably weaker than in the case of the first layer.

While the interpretations of the isotherms are apparently clear, it is much more difficult to explain the changes with temperature. The curves of

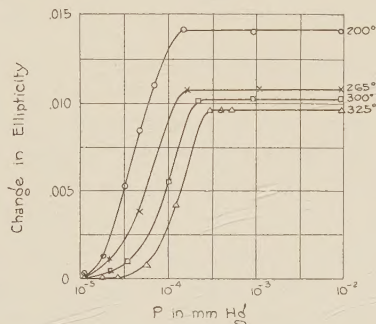


Fig. 5. Adsorption isotherms referred to a common origin.

Fig. 4 seem to show that the surface is clean at 325°C, so that the measured ellipticity must be natural to the clean surface. The increase in ρ with decrease in temperature may be explained in one of two ways. First, as the temperature is lowered, a single layer of water vapor might begin to form which is complete at temperatures around 100°C. This would mean, then, that at high temperatures there is adsorption only of methyl alcohol, but that at lower temperatures adsorption of both methyl alcohol and a layer of water vapor is observed. The second possibility is that there is no water vapor present and that the increase in ellipticity is indicative of an actual surface roughening with lowering of temperature. Very recently, Frazer⁶ has observed the same type of curve with an agreement which is very encouraging. He attributes the increase in ellipticity to an adsorption of air; however, this is rather unlikely. The only possible constituent of air that would be likely to adsorb so strongly would be water vapor. However, there is nothing conclusive to be drawn from the data thus far. Certain modifications in the crystal container will have to be introduced, as it does not now appear that outgassing by heat alone is sufficient to determine whether all traces of water vapor have been removed.

If the effect is actually due to temperature directly, then we can move the curves of Fig. 2 to a common origin at their lowest points as in Fig. 5. This will then give us a family of curves of true adsorption. Then it is possible to calculate the isothermal heat of adsorption by means of the Clausius-Clapeyron equation:

$$\frac{d(\log p)}{dT} = \frac{Q}{RT^2} \quad (4)$$

The approximate values obtained are: 7000 calories for the first layer and 2000 calories for the second layer, in the region of 250°C. However, theoretical considerations seem to be in favor of the first view as the theoretical value of Q is several times larger. If at 325°C the alcohol is adsorbed directly on the salt we could use as a rough approximation the following formula which is due to Nernst:

$$\log p = -\frac{Q}{4.51T} + 3 + 1.75 \log T \quad (5)$$

which, with a value of $p = 10^{-4}$ mm and $T = 600^\circ\text{K}$, yields a value of 40,000 calories per mol. On the other hand one can calculate the energy between an ion and a dipole of moment⁷ P , which is (PeN/r^2) ergs per mol. If we accept for r the value calculated from the hydration of the sodium ion, $r = 1.74\text{\AA}$, for P the value 1.7×10^{-18} ; one again finds for the value of Q about 40,000 calories per mol. On the other hand, we find for 200°C almost the same pressure, which would make Q about 21,000 calories; this decrease can best be accounted for as being due to an adsorption on a partly water covered surface. But the value of 7,000 calories as found experimentally is far too small to account for the vapor pressure as small as 10^{-4} mm at 300°C. One might state the argument in another form. One can expect that the equilibrium pressure of an adsorbed monomolecular layer and the vapor pressure of the substance in bulk to be similar, if the heat of adsorption and the heat of evaporation are similar. Water, with a heat of evaporation of about 9500 calories boils at 100°C; mercury with 13000 calories boils at 338°C. As the equilibrium pressure in the present case is 10^{-4} mm at 325°C, the heat of adsorption must be considerably higher than 13000 calories.⁸

The author wishes to take this opportunity to acknowledge many useful suggestions of Professor A. H. Pfund, concerning the optical set-up; and to express his sincere thanks to Professor Karl F. Herzfeld who has suggested this problem and whose assistance and supervision during its growth have been most helpful.

⁶ J. H. Frazer, *Phys. Rev.* **34**, 645 (1929).

⁷ K. Hojendahl, *Phys. Zeits.* **30**, 391 (1929).

⁸ K. F. Herzfeld, *Kinetische Theorie der Wärme*, p. 298 ff. Vol. 3, Müller-Pouillet, *Lehrbuch der Physik*.

BIOGRAPHY

Shirleigh Silverman, son of Louis and Minerva Kamens Silverman was born in Baltimore, Maryland, on January 12, 1907. His early education was received in the public schools of Baltimore and at the Baltimore City College. He received his A.B. degree from Johns Hopkins University in 1927, and his graduate work has been pursued at the same institution during the years 1927-1928, 1928-1929, 1929-1930. He was a student assistant in Physics during 1927-1928, and an instructor in Physics the following two years. During his three years of graduate work he has attended courses in Physics under Professors K. F. Herzfield, J. C. Hubbard, A. H. Pfund and R. W. Wood, and in Mathematics under Professor F. D. Murnaghan.

